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PATENT SPECIFICATION

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NO DRAWINGS.



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COMPLETE SPECIFICATION.

Improvements in and relating to Membranes.

We, SARTORIUS-MEMBRANEFILTER G.m.b.H. formerly known as Membranfiltergesellschaft G.m.b.H., a German Company, of 96/102, Weender Landstrasse, Goettingen, 5 Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to membranes, more particularly to alginate membranes and to a process for the production of alginate membranes.

15 The known alginate gels are produced by putting a thin layer of an alginate solution on to a porous substrate which is saturated with a solution of a substance which forms an alginate gel with the alginate solution.

20 Such alginate gels are used, for example, as filtering material for the separation of viruses or other minute particles up to a size of less than 10×10^{-3} metres or as so-called ion exchanger membranes in which polyvalent cations, such as aluminium, can

25 be substituted for other ions. The property of the alginate membrane of dissolving again in, for example, solutions of sodium ions makes it possible to obtain a concentrated virus suspension after the filtration.

30 The alginate solution used for the formation of the alginate gel is an aqueous solution of an alkali metal or ammonium salt of alginic acid, a weak organic acid. Preferably solutions of alginate of monovalent cations, for example of sodium are used.

35 Algimates with polyvalent cations (except Mg^{2+}) are insoluble.

40 The gel-forming substance is a salt solution with polyvalent cations, for example with Al^{3+} or La^{3+} cations. Salt solutions with these cations have proved the most useful. When the alginate membranes to

be prepared are to be used for the filtration of germs and viruses, the use of heavy metal ions harmful to germs in the solution is ruled out. Mg^{2+} cations are not utilisable for the gel formation.

45 For the preparation of the alginate gel a porous substrate, for example a paper or membrane filter, is saturated with the gel-forming substance. The viscous alginate solution is drawn out in a thin layer on the foundation by means of a sliding carriage. A reaction takes place in which the polyvalent cations of the gel-forming substance combine with a specific number of alginate chains. The reaction product is 50 insoluble and separates as a thick water-containing gel. The cations of the alginate solution combine with the acid residue of the gel-forming substance to give a water-soluble salt. Owing to diffusion processes and syneresis (shrinkage until adjustment to a thermodynamically stable condition occurs) the gel formed has three zones; (a) 55 a primary membrane which is formed at the boundary between the gel-forming substance on the foundation and the alginate solution spread out on this, (b) the region of the so-called "disintegration in drops" 60 and (c) a capillary layer.

65 When the alginate gel is allowed to dry on the substrate after the drawing out, it first shrinks in a direction perpendicular to the surface. Parallel to the surface it retains its extended form at first, since the primary membrane of the gel is connected firmly with the substrate by adsorption. With progressive drying, however, the tensions parallel to the surface become greater 70 than the adsorptive linkage, so that the alginate gel is detached from the foundation, becomes brittle and tears. For this reason alginate gels could not previously be dried,

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but are kept only in the wet state, i.e. under water. On account of the high water content in comparison with the solid substance, the gel has a very low stability and can only be used with the utmost caution. A fairly long keeping time and transport of the gel are out of the question in practice. These properties of the alginate gel make it necessary that the gel should not be formed until immediately before use and as far as possible at the place of its later use, for example for filtrations, directly in the filtering apparatus.

Through the invention the disadvantages and difficulties hitherto connected with the alginic gels may be avoided. This is achieved according to the invention by mixing a softener with the alginate solution before its application to the substrate and, after the gel-forming process, subjecting the gel and the foundation to a drying process.

When a softener is added to the alginate solution before the gel-formation the softener remains as a dispersing phase of the gel during the drying. Thus the gel does not completely shrink on drying, but remains pliable and consequently firmly connected to the substrate. An alginate membrane partly shrunk and dried in this way is substantially more stable than the gel formed without softener. The partly-shrunk membrane is stable towards air and therefore able to be stored and transported. The stable alginate membranes may be prepared in any desired shape and size and, owing to the firm connection between the alginate membrane and the substrate, the manipulation is much simplified.

The addition of softener does not alter the properties of the alginate membrane. In the optical and electron microscopes the partly shrunk membrane shows the same structure as the gel formed without addition of softener and not dried, since essentially only the capillary layer perpendicular to the surface shrinks. However, the capillarity is not thereby lost, so that the partly shrunk membrane shows, for example, the same permeability and the same capacity of retaining the very smallest particles as a gel prepared without addition of softener and not dried.

The stability of the alginate membrane achieved by the addition of softener is also retained when this is wetted with water during use, since the membrane absorbs hardly any moisture. When the membrane is washed through for a relatively long time, however, for example in the case of filtrations, the softener is washed out by water. Thereupon the partly shrunk alginate membrane on drying is detached from its connection with the substrate, so that it is possible to remove the membrane, together with the filter residue from the substrate. If it

is desired to obtain the membrane wet, it is placed for a short time in a basin with water. After a few moments the membrane floats off the substrate. It is found that filtered viruses are not lost during this operation; they remain in the capillary spaces.

A hygroscopic liquid that is difficultly volatile is preferably used as the softener. It is thus ensured that even on fairly long storage the softener remains in the alginate membrane and the membrane cannot completely dry out, so that the danger of tearing and detachment of the substrate is removed. Glycerol has proved to be especially suitable as a softener. 5 to 20 weight per cent of glycerol is added to the alginate solution during manufacture of the membrane. If the percentage of glycerol is less than this the produced membrane is brittle; if more the membrane is greasy. An addition of 12.5% by weight of glycerol has proved particularly useful.

The invention will be further described with reference to any one of the following Examples.

EXAMPLE 1

An aqueous solution containing about 300 g of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ per litre is used as the gel-forming substance. A sheet of porous filter substrate is saturated with this solution and laid, free from air bubbles, on a flat surface. A 0.5 to 3% aqueous sodium alginate solution serves as the alginate solution. A 1% by weight sodium alginate solution is preferably used. 12.5% by weight of glycerine is mixed with this solution. Less than 5% by weight the prepared membrane remains brittle.

The alginate and glycerol solution is spread over the saturated porous substrate to a thickness of about 1 mm by means of a sliding carriage. An alginate gel now forms, when the trivalent aluminium ions combine with the alginate chains, and Na^+ and Cl^- ions remain in solution. The whole is subjected to an air drying at ambient temperature. Within three days the greater part of the water has evaporated. A stable aluminium-alginate membrane remains firmly connected with the membrane filter foil, which alginate membrane still contains excess $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, some NaCl and glycerine. The membrane filter foil with the alginate membrane firmly adhering thereto can now easily be removed from the flat surface and cut up in a suitable form and stored.

EXAMPLE 2

If instead of AlCl_3 , a solution of about 200 g of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ per litre of water is used as the gel-forming substance, a very dense primary membrane is obtained which

is also thicker than when AlCl_3 is used. Otherwise the alginate membrane does not differ in its structure from that in Example 1.

5. The product formed according to the invention does not have the disadvantages of an alginate gel formed without addition of a softener. The properties required of the alginate gel have not been impaired, 10. however, and the possibilities for its use are not restricted. On the contrary, new possibilities result owing to the stabilised alginate membrane. For example, the alginate membranes prepared according to 15. the process of the invention can also be used in pressure apparatus, while formerly the sensitive alginate gels were destroyed by the pressure of the sealing rings.

WHAT WE CLAIM IS:—

20. 1. Process for the preparation of alginate membranes by the application of a layer of an aqueous solution of an alkali metal or ammonium alginate to a porous substrate saturated with a salt solution containing polyvalent cations that form an alginate gel by reaction with the alginate

solution in which the alginate solution, before application to the substrate, is mixed with a softener and after the gel-forming process, the gel and the substrate are dried by being subjected to a drying process. 30

2. Process as claimed in claim 1, in which the softener is a difficultly volatile hygroscopic liquid. 35

3. Process as claimed in claim 2 in which glycerol is used as the softener.

4. Process as claimed in any one of the preceding claims in which 5 to 20% by weight of the softener is admixed with the alginate solution. 40

5. Process as claimed in claim 4 in which 12.5% by weight of the softener is mixed with the alginate solution.

6. Process for the preparation of alginate membranes substantially as hereinbefore described with reference to any one of the Examples. 45

7. Alginate membranes when prepared by the process of any preceding claim.

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